Chemical Changes in Spray-Dried Skimmilk Held Near Dryer Outlet Temperatures

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Abstract

The hydroxymethylfurfural (HMF) content and fluorescence of spray-dried powders (2.8 to 5.6% H_2O) made from pasteurized skimmilk increased during storage at temperatures similar to those encountered in products held in bulk storage without cooling immediately after drying (37 to 60 C). Rate of increase was directly related to the storage at 50 C, an increase of HMF in powders containing 2.8% H_2O could be detected, the amount originally present doubling during 16 hours of storage. The powders exhibited changes in the pattern of fluorescence excited by ultraviolet light having wavelengths of 330, 360, and 390 mμ. More than a fivefold increase in HMF and a doubling of fluorescence activated at 330 mμ was observed before changes in the visible color of the powder became detectable. Since no significant changes were noted in the powders during one week of storage at 37 C, it was concluded that chemical changes in milk constituents during spray drying can be further decreased by cooling powder to this temperature immediately after drying.

In some spray-drying plants large containers are being used to collect and store nonfat dried milk (NDM) before packing it for distribution. These large masses of powder lose heat slowly and much of it is exposed to elevated temperatures for considerable periods of time.

The question of the possible adverse effect of this practice of powder handling on product quality is being raised by some individuals engaged in milk powder purchasing and quality control. We therefore wish to present data showing extent of some of the chemical changes that occur in NDM when held at temperatures near those reached by the powder in the final stages of drying.

Our work is concerned only with 5-hydroxymethylfurfural (HMF), fluorescence, and color of the dried skimmilk. Work by other investigators has already demonstrated that these properties are indicators of the extent of heat-induced chemical change in dairy products (7, 14).

Experimental Procedures [1]

Mixed herd milk obtained from the Agricultural Research Center, Beltsville, Maryland, was separated at 4 C. The skimmilk obtained was pasteurized by holding for 15 sec at 165 C in a tubular heat exchanger, then concentrated to 45-47% total solids in a Harris-Wiegand type falling film evaporator and finally dried, using a 9-ft Swenson dryer modified for foam-spray drying as previously described (4).

The moisture content of the finished powder, as determined by codistillation with toluene (10), was varied by systematically controlling the temperature of the air entering the dryer intake during drying.

All powder samples were then immediately air packed in no. 1 cans, and individual series of samples containing graded moisture contents were stored in ovens whose temperatures were set to provide a range of storage temperatures between 37 and 60 C.

At appropriate time intervals during holding at elevated temperatures, samples were withdrawn from the ovens, cooled, and analyzed.

The extent of the visible browning of the samples was determined by measuring the amount of light of wavelength 415 mμ reflected from a smooth surface formed by the milk powder. The measurement was made using a Beckman Model B spectrophotometer equipped with that company's reflectance-measuring accessory. A surface formed from unheated milk powder was used as the reference standard.

The fluorescent materials in NDM powder were studied using an Aminco-Bowman Spectrophotofluorimeter equipped with crossed Nicol prisms. Samples were prepared for analysis by adding 2 ml of 0.5 M potassium oxalate to 10 g of milk powder and bringing the mixture up to 100 ml final volume by addition of distilled water. After standing for 30 min at room temperature the suspensions were centrifuged for 30 min at 40,000 rpm in a Spinco Model L centrifuge.

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[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

The total HMF content of the NDM samples under investigation was determined using the method published by Keeney and Bassette (7).

Results

Samples of NDM, containing 2.8 and 3.2% water, showed no significant change in color during holding for one week at temperatures ranging up to 60 C. However, when the moisture content of the powder was increased to 4%, definite increases in the amount of light absorption at 415 mμ, indicative of browning, were observed as the samples were held for increasing periods at 60 C as shown in Figure 1. The rate of this color change at 60 C increased rapidly when the moisture content of the NDM was raised to 5.2%, as shown in Figure 2. No change in the color intensities of these high moisture samples was observed if the holding temperature was reduced to 37 C.

Even though NDM containing 4% moisture showed little color change during extended holding at 50 C, the fluorescence of the powder increased rapidly. Figure 3 demonstrates the extent of this charge. The plot is based on the existence of materials in NDM having three characteristic activation and fluorescent wavelengths.

It was noted that as the moisture content of the powder was increased above 4% the fluorescence, activated by light of 330 mμ wavelength, reached a maximum during the holding period and then decreased as shown in Figure 4. Similar results were also observed by increasing the holding temperature. Decreasing the holding temperature to 37 C prevented any significant change in the fluorescence pattern of the NDM samples investigated.

The HMF content of the NDM increased rapidly on holding if the temperature exceeded 43 C, as shown in Figure 5. The rate of this change was also increased with increased moisture content of the NDM, as shown in Figure 6. From these two figures it can be seen that low moisture powders undergo substantial change in HMF content during 16 hours of holding at 50 C. If the holding temperature is reduced to 37 C, NDM undergoes no significant increase in HMF, even though its moisture content is increased to 4%. Further study showed that, even at a moisture content of 5.2%, the HMF content of NDM increased only two

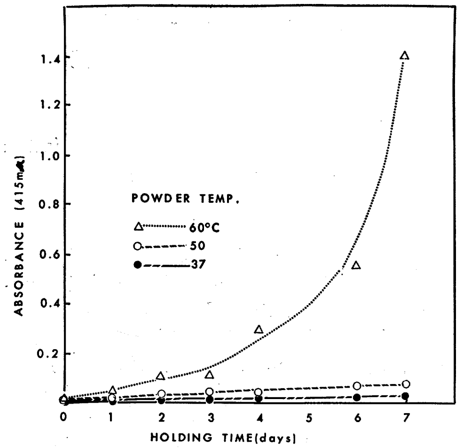

FIG. 2. Effect of powder holding temperature on brown color development in conventional spray-dried NDM containing 5.2% moisture. Moisture content increased by dropping inlet air temperature below that described in legend of Figure 1.

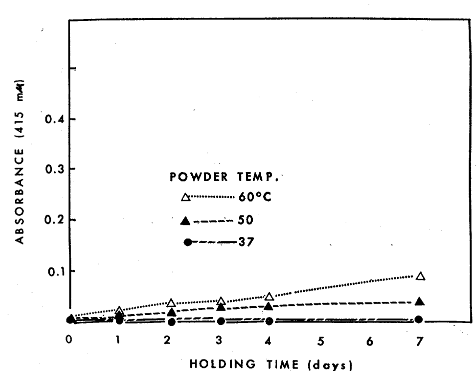

FIG. 1. Effect of powder holding temperature on brown color development in conventional spray-dried NDM containing 4.0% moisture. Material dried using 1.02-mm nozzle and 102-atmospheres pressure in feed line. Inlet air temperature, 122 C.

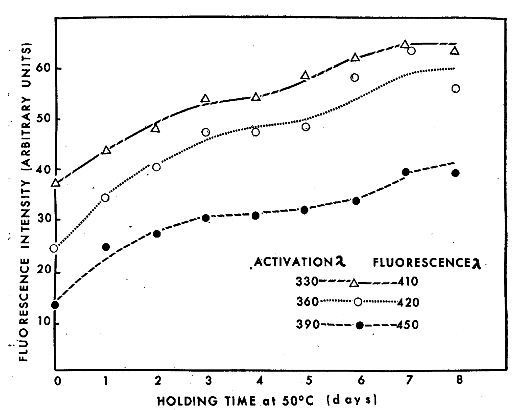

FIG. 3. Effect of powder holding temperature on fluorescence of conventional spray-dried NDM containing 4% moisture prepared as described in legend of Figure 1.

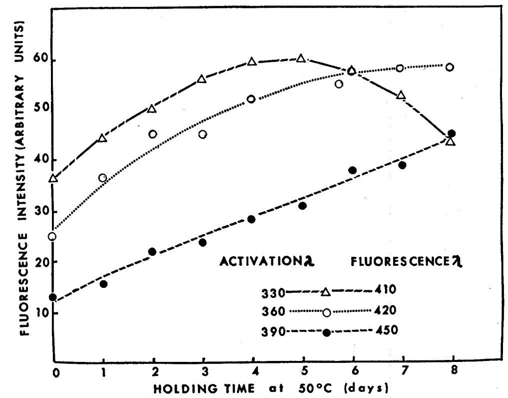

FIG. 4. Effect of powder holding temperature on fluorescence of conventional spray-dried NDM containing 5.2% moisture prepared as described in legend of Figure 2.

micromoles/liter reconstituted milk during one week of holding at 37 C.

The physical form of the NDM had little influence on the rate of HMF formation during holding at elevated temperatures. Figure 7 shows the increase in HMF in foam-spray-dried powders held under conditions conducive to its formation.

Discussion

It is well known that the temperature of NDM as delivered from most spray dryers usually exceeds 37 C. It is also common knowledge that the hot powder, packed in bags or barrels, cools slowly. This holding at elevated temperatures has not been considered deleterious to the maintenance of powder quality (2). No

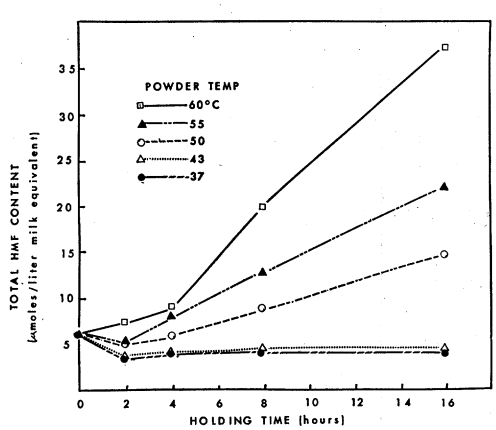

FIG. 5. Effect of powder holding temperature on HMF content of conventional spray-dried NDM containing 4.0% moisture prepared as described in legend of Figure 1.

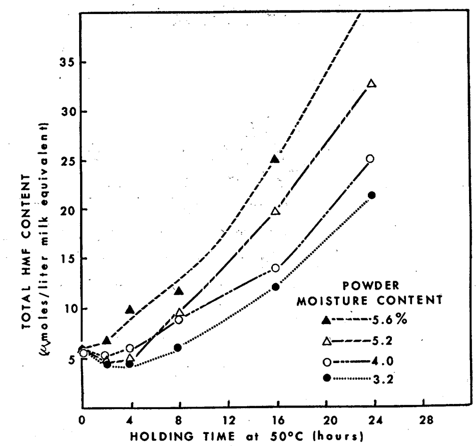

FIG. 6. Effect of powder moisture content on amount of HMF in conventional spray-dried NDM held at 50 C after drying. General production conditions described in legend of Figure 1 were used. Moisture content increased by systematically dropping inlet air temperature from approximately 132 to 107 C during the course of the production run.

real evidence to substantiate this position can be found in the scientific literature.

Our data demonstrate that visible change in NDM held at elevated temperatures immediately after drying is insignificant unless the powders have moisture contents of 4% or more and the holding temperature exceeds 50 C for more than 24 hours. However, the observed lack of color change serves as a poor indicator of lack of chemical change in the product when holding at high temperatures. More refined methods of analysis show that chemical change is actually occurring under these conditions.

Tarassuk and others (11, 14) have correlated

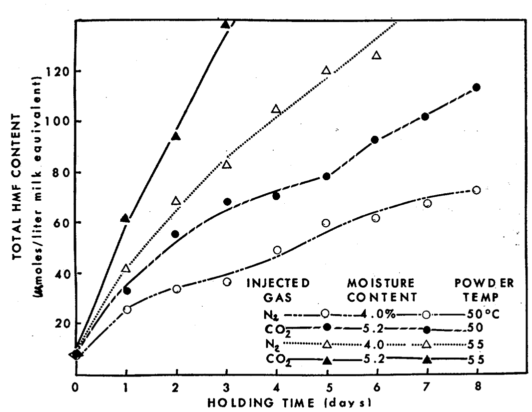

FIG. 7. Effect of powder moisture content and holding temperature on NDM made by use of foam-spray-drying techniques (4).

the amount of material producing fluorescence in milk with the heat treatment received by this product. The fluorescence we have observed in the NDM, held hot, is activated by the same wavelengths of light that activate fluorescence in heated model systems containing casein and lactose (8). We therefore believe that this fluorescence arises from those Maillard reaction products that serve as precursors for the visible, dark-colored pigments which appear in dairy products that have undergone browning (11).

Further evidence for this can be obtained from the results of our HMF analyses. The appearance of this material in heated milk has already been demonstrated by Potter and Patton (12), and its relation to the Maillard-type browning reaction has been substantiated by Hodge and Rist (5). From Figure 5 it is apparent that substantial increases in HMF concentration will occur in milk powders containing 4% moisture if held at temperatures higher than 43 C for only eight hours. At 60 C measurable change in HMF content occurs within two hours. In general, high moisture content and high temperature holding favor the development of HMF. The levels of HMF we observed in our fresh powders are similar to those reported by Keeney and Bassette (7). The highest HMF concentrations we observed in powders held for 24 hours at elevated temperatures were similar to those reported in off-flavored NDM by these same investigators. Data published by Craig et al. (3) indicated that high HMF content of vacuum foam-dried whole milk powders could be associated with poor flavor stability during storage. Brownley and Lachman (1) have also associated the presence of HMF in spray-dried lactose with rapid browning of the product during normal storage.

While it is obvious from our data that NDM, especially of higher moisture content, undergoes measurable chemical change within a few hours if held at temperatures of 50 C or higher, some questions may arise as to how this relates to conditions found in actual commercial plant practice. No information is published on the temperatures of milk powder at the time of manufacture, after packaging and during the first stages of storage.

The early literature on spray drying usually states that the temperature of the powder particles will not exceed the wet bulb temperature of the air in the dryer. Marshall (9) has stated that this could hold only for drops of pure liquids. During the early stages of drying of drops of liquid containing dissolved material, the drop temperature can be estimated from a psychrometric chart as being near the point where the adiabatic saturation line drawn through the air drying conditions crosses the curve for the vapor pressure of the solution saturated with the nonvolatile materials it contains (13). During the terminal stages of drying, the temperature of the evaporating drop or particle rapidly rises, to compensate for the marked depression in the vapor pressure of the residual water, and the temperature driving force decreases to zero. The surface temperature of the drop must then approach that of the surrounding air.

The finished powder temperature is also influenced by the dryer design and operating conditions. Those dryers which separate the powder from the drying air slowly and which are operated at relatively high temperatures must necessarily produce hotter powders.

The temperature of the powder produced by our dryer operating at an air intake temperature of 140 C at outlet temperature of 75 to 85 C is approximately 60 C. If cooled slowly from this temperature our NDM would undergo chemical changes measurable as described in this paper.

If the bulk handling practices used in present-day plants expose newly made powder to elevated temperatures for more than a few hours immediately after manufacture, a powder cooler capable of reducing powder temperature to 37 C, or lower, would seem to be required to maintain product quality. This would, of course, hold only where low-heat powders are required for beverage or other specific food use.

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